UNIVERSITY OF PENNSYLVANIA

THE QUANTITATIVE SEPARATION OF GERMANIUM AND ARSENIC

HAROLD J. ABRAHAMS

A THESIS

IN CHEMISTRY

PRESENTED TO THE FACULTY OF THE GRADUATE SCHOOL IN

PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR

THE DEGREE OF DOCTOR OF PHILOSOPHY

PHILADELPHIA

1932

THE QUANTITATIVE SEPARATION OF GERMANIUM AND ARSENIC

A THESIS

IN CHEMISTRY

PRESENTED TO THE FACULTY OF THE GRADUATE SCHOOL OF THE UNIVERSITY OF PENNSYLVANIA IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

HAROLD J. ABRAHAMS

PHILADELPHIA

1932

ACKNOWLEDGMENT

This study was suggested by, and pursued under the direction of Dr. John H. Müller, for whose encouragement, invaluable suggestions and advice the author is deeply grateful.

R. UNIV.
BIBLIOTHEEK
LEIDEN

THE QUANTITATIVE SEPARATION OF GERMANIUM AND ARSENIC

By Harold J. Abrahams

The quantitative separation of germanium from arsenic is attended by considerable difficulty, a fact which is not surprising in view of their relative positions in the periodic arrangement of the elements. As these two elements are so universally associated in germanium bearing minerals, this separation has been made the subject of several investigations in the past. As early as 1886 Winkler[1] suggested a means of effecting this separation through the mixed sulfides. According to this method, both elements are taken into alkaline solution as thio compounds, and the solution neutralized with acid, a slight excess of acid then being added to bring about complete reprecipitation of the arsenic sulfide. This method depends upon the existence of a soluble alkali thiogermanate and the stability of hypothetical thiogermanic acid in a solution, the hydrogen-ion concentration of which is sufficient to decompose the thioarsenite quantitatively. The arsenic sulfide thus formed is removed by filtration, and the germanium is recovered from the filtrate. Truchot[2] mentions the same separation. No analytical data are given by either author.

Dennis and Papish[3] have described a method for the preparation of pure germanium tetrachloride from a mixture containing arsenic and germanium by distilling the mixture with hydrochloric acid in a current of chlorine. The pentavalent arsenic which results is completely non-volatile under the conditions of this process. Dennis and Johnson,[4] who have investigated this excellent means of separating arsenic from germanium, state that, if their column still is used, 83% of the germanium is obtained in the first distillation, and 16% from the residue by later runs.

Various modifications[5] of this method have appeared in which strong oxidizing agents, such as potassium dichromate, etc., have been added to the hydrochloric acid to maintain arsenic in the pentavalent condition.

[1] Winkler, *J. prakt. Chem.*, **142,** 194 (1886).
[2] Truchot, "Les Terres Rares," Paris, **1898.**
[3] Dennis and Papish, *J. Am. Chem. Soc.*, **43,** 2131 (1921).
[4] Dennis and Johnson, *ibid.*, **45,** 1380 (1923).
[5] Browning and Scott, *Am. J. Sci.*, **46,** 663 (1918).

A separation based upon the failure of germanium sulfide to precipitate in the presence of hydrofluoric acid has been proposed by Müller.[6] In this method the separation of germanium and arsenic proceeds without difficulty, but the recovery of germanium in a weighable form from the very stable fluogermanic acid is difficult.

The purpose of the present investigation was to study a separation based upon the selective precipitation of arsenic, by hydrogen sulfide, from solutions containing both elements in the presence of a controlled amount of free acid.

Preliminary Experiments

It is a well known fact that germanium sulfide separates practically completely from an aqueous solution of the dioxide when treated with hydrogen sulfide, if the hydrogen-ion concentration is sufficiently high. Concerning the mechanism of this reaction, it is believed that, in the presence of sufficient acid, germanic cations reach a concentration which permits precipitation of germanium sulfide. In the absence of the limiting hydrogen-ion concentration, however, hydrogen sulfide is entirely without effect on such a solution over many hours. To determine the limiting value of acidity necessary for the first separation of germanium sulfide, the experiments shown in Table I were made. Sulfuric acid was used as the free acid because small amounts of this acid retained in the precipitated germanic sulfide did not interfere with the ultimate conversion to dioxide.

Experiments 1a to 12c Inclusive.—Table I shows in brief the effect of hydrogen sulfide upon solutions of pure germanium dioxide, under varying conditions of free acid concentration. These results indicate that no precipitation of germanium sulfide takes place until the acid concentration exceeds 0.09 *N*.

In all experiments it was necessary to add 1 g. of ammonium sulfate as suitable electrolyte in order to prevent colloidal dispersion of any arsenic sulfide, under existing conditions of low acid concentration. Preliminary experiments indicated that the presence or absence of ammonium sulfate had no effect upon the action of hydrogen sulfide in the case of solutions containing only germanium dioxide. It may be noted that sulfuric acid was used throughout as the free acid and ammonium sulfate as electrolyte, because, unlike hydrochloric acid and its corresponding salt, these reagents could not form any volatile germanium compound.

Experiments 12a, b and c indicate that free hydrochloric acid and ammonium chloride may be substituted for sulfuric acid and ammonium sulfate without any observable change in precipitation effect, but chlorides were purposely avoided in quantitative work for reasons given above.

[6] **Müller**, *J. Am. Chem. Soc.*, **43**, 2549 (1921).

TABLE I

PRELIMINARY EXPERIMENTS. EFFECT OF HYDROGEN SULFIDE ON GERMANIC OXIDE SOLUTIONS UNDER VARYING ACID CONCENTRATION

No	Vol., cc.	GeO_2, mg.	As_2O_3, mg.	Final acid normality	Hours	Results	Remarks
1a	52.2	250	..	0.008	16	Faint turbidity	Turbidity, sulfur; no GeS_2
1b	52.2	25	..	.008	16	Clear	
2a	54.4	250	..	.016	18	Faint turbidity	Turbidity—sulfur
2b	54.4	25	..	.016	18	Unchanged	
3a	56.4	250	..	.023	..	Faint turbidity	1 g. $(NH_4)_2SO_4$ added
3b	56.4	25	..	.023	..	Unchanged	
4a	57.5	250	..	.026	19	Faint turbidity	
4b	57.5	25	..	.026	19	Unchanged	
5a	58.7	250	..	.030	20	Faint turbidity	
5b	58.7	25	..	.030	20	Unchanged	
6a	60.7	250	..	.035	21	Faint turbidity	
6b	60.7	25	..	.035	21	Unchanged	
7a	62.9	250	..	.041	21.5	Faint turbidity	
7b	62.9	25	..	.041	21.5	Unchanged	
8a	65.1	250	..	.046	22	Faint turbidity	
8b	65.1	25	..	.046	22	Unchanged	
9a	67.3	250	..	.051	23	Faint turbidity	
10a	50.0	125	..	1.0	5 min.	Heavy ppt.	Dense ppt. (GeS_2) overnight
10b	50.0	125	..	0.5	10 min.	Heavy ppt.	
10c	50.0	125	..	.25	2	Little ppt.	
10d	50.0	125	..	.125	2	Turbid	
11	50.0	125	..	.09	48	Unchanged	
12a	50.0	125	..	.1 (HCl)	48	Faint turbidity	1 g. NH_4Cl added
12b	50.0	125	..	.05(HCl)	48	Unchanged	1 g. NH_4Cl added
12c	50.0	125	..	.025(HCl)	48	Unchanged	1 g. NH_4Cl added
13a	50.0	...	31	..	24	As_2S_3 pptd.	1 g. $(NH_4)_2SO_4$ added
13b	50.0	...	31	.004	24	As_2S_3 pptd.	1 g. $(NH_4)_2SO_4$ added.
13c	50.0	...	31	.008	24	As_2S_3 pptd.	Ppt. more satisfactory than in a
13d	50.0	...	31	..	24	As_2S_3 colloidal	
13e	50.0	...	1	..	24	As_2S_3 pptd.	1 g. $(NH_4)_2SO_4$ added
13f	50.0	...	1	.004	24	As_2S_3 pptd.	1 g. $(NH_4)_2SO_4$ added
14a	50.0	10	1	.004	16	As_2S_3 pptd.	1 g. $(NH_4)_2SO_4$ added
14b	50.0	50	1	.004	16	As_2S_3 pptd.	1 g. $(NH_4)_2SO_4$ added
14c	50.0	125	1	.004	16	As_2S_3 pptd.	1 g. $(NH_4)_2SO_4$ added
15a	77.0	375	0.5	.004	1	As_2S_3 pptd.	1 g. $(NH_4)_2SO_4$ added
15b	77.0	375	1	.004	1	As_2S_3 pptd.	1 g. $(NH_4)_2SO_4$ added
16a	92.2	375	1	.033	3	As_2S_3 did not settle	Ppt. completely removed by filtration. Filtrate gave snow-white GeS_2
16b	92.1	375	0.5	.033	16	As_2S_3 did not settle	
16c	62.2	250	1	.032	3	As_2S_3 did not settle	
16d	117.1	375	0.5	.068	16	As_2S_3 did not settle	
16e	124.4	500	1	.032	3	As_2S_3 did not settle	

Experiments 13a to 13f concern the effect of hydrogen sulfide on solutions containing arsenic in absence of germanium.

Experiments 14a, b and c were duplications of 13e and f with the exception that they contained approximately 10, 50 and 125 mg. of germanium

dioxide in addition. They were saturated with hydrogen sulfide overnight, whereupon all arsenious sulfide was found at the bottom of the flask in a granular condition. The volume of the precipitated arsenious sulfide, on comparison with a standard, seemed to indicate little or no removal of germanium. This behavior was given a more rigorous test by setting up experiments 15a and b: 15a contained 0.5 mg. of arsenious oxide, 1 g. of ammonium sulfate, 1.5 cc. of 0.2 *N* sulfuric acid, and 375 mg. of germanium dioxide (total volume 77 cc.); 15b contained 1 mg. of arsenious oxide but was otherwise identical with 15a. On saturating with hydrogen sulfide, finely divided but filterable arsenious sulfide appeared in each case. Expts. 16a to e, with mixtures of the two oxides, in the ratios of 1 arsenious oxide to 375 germanium dioxide, and 1 arsenious oxide to 750 germanium dioxide, were then made. These solutions contained 1 g. of ammonium sulfate and varied in acid concentration from 0.03 to 0.06 *N*. While the arsenious sulfide in these experiments did not settle, it could be removed perfectly by filtration. The germanium sulfide precipitated in the filtrate was snow white. (The limit of acidity for the non-precipitation of germanium is 0.09 *N*, as shown by experiments 10 and 11.)

Quantitative Analysis of Mixtures

The investigation was now made quantitative by making mixtures of known concentrations and analyzing them in the light of the knowledge gained from the experiments discussed above. Mixtures each containing 242 mg. of germanium dioxide but varying in arsenious oxide content from 50 to 1.1 mg. and one mixture containing 484 mg. of germanium dioxide to 1.1 mg. of arsenious oxide were made. They were then analyzed by the following procedure. To the mixtures measuring 60 to 70 cc., 3 cc. of approximately 0.1 *N* sulfuric acid and 1 g. of ammonium sulfate were added and the mixtures saturated with hydrogen sulfide in a closed system under pressure. The arsenic sulfide was filtered off, washed thoroughly with hydrogen sulfide water containing ammonium sulfate, and determined as magnesium pyroarsenate, by dissolving in the minimum amount of ammonia, oxidizing with hydrogen peroxide, boiling to destroy the excess of the latter, and then following the recommendation of McNabb.[7]

The filtrate from the arsenic sulfide was made 6 *N* with sulfuric acid and the germanium sulfide precipitated in the usual way. The sulfide was filtered upon a small glass filtering crucible (capacity about 15 cc.). A part of the filtrate was resaturated with hydrogen sulfide, while the rest of the filtration was being carried out. This solution was used in removing any precipitate adhering to the precipitation flask. The precipitate was sucked down as dry as possible and washed with a few cc. of 2 to 3 *N* sulfuric acid saturated with hydrogen sulfide.

The germanium was determined by hydrolytic conversion of the sulfide to dioxide as follows. The small glass filter containing the sulfide was introduced into a weighed quartz beaker containing enough boiling water to cover completely the filter crucible and its contents. The water was kept actively boiling and a cover glass was used to exclude air as far as possible. This is necessary to prevent oxidation of escaping hydrogen sulfide and consequent separation of free sulfur. Boiling was continued until the whole of the precipitate had passed into clear solution, indicating completion of the hydrolysis of the sulfide. The glass filter crucible was now removed and washed free of

[7] McNabb, *J. Am. Chem. Soc.*, **49**, 1451 (1927).

adhering solution. At this point the weighed quartz beaker contained nothing but germanic oxide solution and perhaps traces of free sulfur. Evaporation was continued to near dryness, at which stage a small amount of pure nitric acid was added, and evaporation then continued to complete dryness. The dioxide resulted upon ignition.

It was noted that several treatments with nitric acid were required in case of accidental separation of appreciable amounts of free sulfur, but complete exclusion of air, especially during the initial hydrolysis of the sulfide, or in its precipitation made this unnecessary.[8]

TABLE II

QUANTITATIVE SEPARATION OF GERMANIUM AND ARSENIC

	As_2O_3 taken, g.	Found, g.	GeO_2 taken, g.	Found, g.
1	0.0500	0.0498	0.2417	0.2412
2	.0500	.0503		
3	.0250	.0249	.2417	.2413
4	.0250	.0251		
5	.0125	.0125	.2417	.2415
6	.0125	.0125		
7	.0062	.0064	.2417	.2420
8	.0011	.0013	.2417	.2415
9	.0011	.0008	.4840	.4834

Table II shows clearly that the described separation of germanium and arsenic is satisfactory for mixtures containing large amounts of germanium and small amounts of arsenic, and that the separation can be effected in a single operation.

From all the qualitative and quantitative experiments with mixtures of arsenic and germanium sulfides, it was observed that very small amounts of arsenic show an unexpected tinctorial effect upon the snow-white germanic sulfide. It is of interest to investigate the minimum amount of arsenic sulfide which would produce an observable effect on the appearance of germanium sulfide. To this end four standards were made, each containing 121 mg. of germanium dioxide, 1 g. of ammonium sulfate and 4.5 cc. of concentrated sulfuric acid, the total volume of each being about 30 cc. Mixture (a) contained 0.28 mg. of arsenious oxide in addition, mixture (b) 0.17 mg. of arsenious oxide, mixture (c) 0.11 mg. of arsenious oxide, and mixture (d) 0.06 mg. These standard mixtures were saturated with hydrogen sulfide: (a) and (b) showed a distinct yellowness, (c) and (d) appeared yellow by comparison with a white surface, or standard precipitate of pure germanic sulfide. From the above it is seen that any quantity of arsenic contaminating the germanium in excess of about 0.2% will be observable by simple inspection.

Mixtures containing large amounts of arsenic and small amounts of germanium and mixtures of equal quantities of both elements were next investigated.

[8] A detailed study of the hydrolytic conversion of germanium sulfide to germanium dioxide will appear in a separate paper by Müller and Eisner, *Ind. Eng. Chem., Anal. Ed.*, January, 1932.

Three mixtures of approximately the same germanium dioxide and arsenious oxide content were made—A, B and C. "A" contained 242 mg. of germanium dioxide, 250 mg. of arsenious oxide, 2 g. of ammonium sulfate and 1 cc. of *N* sulfuric acid (total volume of 103 cc.). B was identical with A, but was further diluted with 50 cc. of water (the total volume being 153 cc.). C was identical with B. All were saturated with hydrogen sulfide for two hours. C was raised to almost boiling and so maintained while the gas was bubbled through. Experiment B afforded an opportunity to observe any advantage due to greater dilution. The results obtained were poor, as A, containing 242 mg. of germanium dioxide, permitted the recovery of but 232.6 mg. B and C were correspondingly low by approximately 6 mg.

It was probable that the large volume of the arsenic sulfide prevented thorough removal of germanium dioxide solution during the washing process in experiments A, B and C. The analyses were therefore repeated with one-half the quantity of each oxide, though the total volume remained at 150 cc. The quantity of *N* acid was reduced to 0.5 cc. and the precipitates were washed by decantation. "C," as previously, was saturated at elevated temperature. Results are shown in Table III.

Removal of any germanium sulfide present in the arsenious sulfide next suggested itself. Mixtures of the oxides were made, diluted to 150 cc. and 1 g. of ammonium sulfate and 0.5 cc. of *N* sulfuric acid added. The mix-

TABLE III

EXPERIMENTAL RESULTS

	GeO_2 taken, g.	Found, g.	As_2O_3 taken, g.	Found, g.
A	0.1210	0.1200	0.1250	0.1260
B	.1210	.1201	.1250	.1261
C	.1210	.1215	.1250	.1255

tures were saturated with hydrogen sulfide and the precipitates washed by decantation. These precipitates, consisting of arsenic sulfide containing traces of germanic sulfide, were redissolved in a minimum quantity of ammonia (1:2) and the solution diluted to about 150 cc. *N* sulfuric acid was then carefully added, with constant stirring, until the solution was neutral, then enough excess acid to make the medium between 0.05 and 0.1 *N*. This procedure is a modification of the old method originated by Winkler and mentioned by Truchot and depends upon the relative stability of hypothetical thiogermanic acid. The mixture was saturated with hydrogen sulfide and filtered. This small amount of germanium dioxide held by the arsenious sulfide is evidently quantitatively recoverable, as shown in Table IV. The germanium dioxide in the filtrate was determined separately in order to learn the amount of the germanium sulfide held by the arsenic sulfide. Results are shown in Table IV.

TABLE IV

EXPERIMENTAL RESULTS

	GeO_2 taken, g.	Found, g.	As_2O_3 taken, g.	Found, g.
1	0.1210	0.1205	0.1250	0.1252
2	.1210	.1206	.1250	.1247
3			.1250	.1254

The germanium dioxide removed from the arsenious sulfide was found to weigh 0.3 mg.

Analysis was then made of mixtures containing 125 mg. of arsenious oxide and amounts of germanium dioxide varying from 1.3 to 60.5 mg., with the results given in Table V.

TABLE V

EXPERIMENTAL RESULTS

	GeO_2 taken, g.	Found, g.	As_2O_3 taken, g.	Found, g.
1	0.0012	0.0013	0.1250	0.1250
2	.0062	.0066	.1250	.1254
3	.0120	.0122	.1250	.1254
4	.0302	.0299	.1250	.1249
5	.0605	.0602	.1250	.1250

The germanium dioxide contents of Nos. 1, 2 and 3 were determined by dissolving germanium sulfide in ammonia, collecting in a weighed crucible, oxidizing with a few drops of hydrogen peroxide, evaporating and carefully igniting. This procedure was followed because the quantities were small. For the estimation of the larger quantities of germanium dioxide, the method of hydrolytic conversion to oxide was used.

From final results as shown in Table V, it may be concluded that higher dilution of the solution of the mixtures containing relatively large amounts of arsenic favors the more complete separation of these elements (see Table IV). Further treatment of the precipitated arsenic sulfide as described is necessary if the arsenic exceeds 15–20% in the mixture.

As all of the above described separations have dealt with simple mixtures of the pure oxides of germanium and arsenic, it was thought advisable to extend this method of separation to a naturally occurring arsenical germanium compound. Germanite was selected for this purpose because its composition is of special interest and only a few analyses of this mineral have been heretofore reported.[9]

Analysis of Germanite

A carefully selected sample of germanite which was free from any visible occluded mineral was analyzed for total constituents, making use of the method herein described for the separation and determination of arsenic and germanium.

[9] Pufahl, *Metall u. Erz*, **19**, 324 (1922); Kriesel, *ibid.*, **20**, 357 (1923); *Chem.-Ztg.*, **48**, 961 (1924); Thomas and Pugh, *J. Chem. Soc.*, **125**, 816 (1924); Todd, *Min. Toronto Studies*, **17**, 62 (1924).

A 3-g. sample of the finely divided mineral was oxidized by repeated evaporation with nitric acid in the presence of sulfuric acid, and the opened-up material thus obtained was treated with a large excess of hydrochloric acid. Distillation was carried out until all germanium and much of the arsenic had been collected in the acid distillate. The latter was analyzed as described. The following results were obtained by total analysis.

Ge	7.37	Zn	2.87
As	3.92	Pb	0.71
Cu	45.38	S	30.96
Fe	5.89	W	0.10
Ga_2O_3	0.68	Gangue	1.47
Al_2O_3	0.13	Total	99.48

Recalculation of these values on the assumption that the small amounts of aluminum, gallium, zinc, lead, arsenic, tungsten and siliceous gangue are independent constituents indicates the probable composition of this mineral to be $7CuS \cdot FeS \cdot GeS_2$.

Summary and Conclusions

1. Germanium and arsenic are shown to be quantitatively separable by a simple precipitation of the sulfides, under regulated conditions of free acid concentration.

2. Small amounts of arsenic can be removed completely from large quantities of germanium in a single operation. Relatively large quantities of arsenic require a retreatment of the precipitated sulfide to recover traces of occluded or co-precipitated germanium sulfide.

3. Very small quantities of arsenic sulfide are shown to have marked coloring effect upon pure white germanium sulfide. This coloring effect is quantitatively studied.

4. Complete analysis of a selected sample of the mineral germanite is appended.